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Treatment of Organic Hazardous Wastes with Ozone and Ultraviolet Radiation

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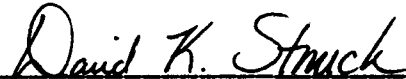92-18384

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A Hydrazine Waste Water Treatment System (HWWTS) has been designed and constructed for the purpose of treating waste waters contaminated by hydrazine propellants generated during space launch operations at Vandenberg AFB. This system utilizes ozone and ultraviolet radiation to reduce the propellant contaminants (and chemical intermediates formed from them during treatment) to innocuous products. In this report, the treatment of other organic wastes, generated during routine operations, is considered. Of particular interest are alcohols (methyl and isopropyl), chlorinated hydrocarbons (trichloroethylene and 1,1,1-trichloroethane), and aromatic wastes (benzene and toluene). The literature was reviewed for each of the materials of interest. Experiments were also carried out for each of the materials. The results of these studies indicate that the alcohols (and, most likely, a variety of other water soluble organic materials) should be readily treatable in the HWWTS. Other organics that are sparingly soluble in water, such as the chlorinated hydrocarbons and aromatics investigated here, should also be treatable. Treatments of chlorinated hydrocarbons and aromatics could generate low levels of gas emissions, averaging 0.05-0.08 lb/hr during the treatment time, due to the low water solubility and high volatility of these materials. Even these figures are likely to be worst case emissions, for reasons discussed herein.

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I. Introduction

Air Force Space Systems Division initiated an R&D program in 1985 to develop an environmentally acceptable method for the detoxification of hydrazine contaminated waste waters generated during space launch operations. This effort has culminated in the fabrication of a prototype Hydrazine Waste Water Treatment System (HWWTS) utilizing ozone and ultraviolet (uv) radiation. The HWWTS, constructed for use at the water treatment facility at Vandenberg AFB, was designed to treat an estimated 300,000 gal of waste water annually that contains low concentrations of hydrazine propellants. Such wastes are generated during launch as well as routine handling and transfer operations and inadvertent spills.

The need for this system has arisen because earlier treatment systems, such as those utilizing hydrogen peroxide or hypochlorite, are now inadequate, due to increasingly stringent federal, state, and local regulations regarding storage and treatment of hazardous wastes. Thus, treatment with hydrogen peroxide produces nitrosamines, known animal carcinogens. Hypochlorite treatment generates chlorinated hydrocarbons, in particular, chlorinated methanes, which are on the U. S. Environmental Protection Agency's list of priority pollutants.

Off-site treatment of wastes is expensive at $4 per gallon (ref. 1), and future costs can be expected to escalate upwards. This is especially true when combustion is selected as the treatment method, in view of rising fuel costs. Moreover, under current regulations, the USAF as the generator of the waste would have perpetual responsibility for that waste, even if treated off site by a waste hauler. The Illinois Institute of Technology Research Institute has estimated the USAF can realize significant cost savings, ranging into millions of dollars over a 20 year lifetime, by on-site treatment in the HWWTS (ref. 1).

While the HWWTS has been designed and built for treatment of hydrazine propellant wastes, it was anticipated that other hazardous wastes generated at Vandenberg AFB might also be treated. Indeed, these ideas have been expressed in recent letters from H. H Takimoto of the Chemical Systems Directorate (see Appendix A) and Colonel O. G. Robertson from Vandenberg AFB (see Appendix B). The ability to treat waste waters containing trace quantities of hazardous wastes other than hydrazines would be highly beneficial and could result in cost savings even greater

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than those cited above. This document considers the feasibility of treating such wastes.

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II. Hazardous Waste Treatment

  A. Experimental

    1. Oxidation in the HWWTS

The HWWTS consists of twin stainless steel tanks capable of treating
up to 2,500 gal of water containing low concentrations of hazardous
wastes. Oxygen containing up to 6% ozone is bubbled through these tanks
at rates up to 30 cfm. The water is recirculated in the tanks and also
passes through units containing a bank of uv lights and tungsten. The
tungsten is used as a catalyst in the system to aid in the decomposition
of small amounts of nitrosodimethylamine that are generated during the
treatment of monomethyl hydrazine and especially during the treatment of
unsymmetrical dimethylhydrazine.

Ozone by itself attacks and destroys hydrazines, as well as any
other organic materials in the system. In the presence of uv light,
dissolved ozone is dissociated into molecular oxygen and singlet D oxygen
atoms (refs. 2,3). These atoms react rapidly with water to produce
hydroxyl radicals. Hydroxyl radicals can also be produced by the
hydroxyl ion catalyzed decomposition of ozone in alkaline solutions
(ref. 4). The hydroxyl radicals [as well as other intermediate radicals
formed in the system (refs. 4,5)] react rapidly with hydrazines and other
organics in the system. All of these processes are likely to contribute
to the overall destruction of hazardous wastes. Which process is likely
to dominate depends on the particular molecule being attacked, as well as
process parameters such as the intensity of the uv light and pH.

The literature data (see below) indicate that in most cases, the
direct reactions between ozone and the hazardous wastes of interest are
too slow to be of significance. Conversely, the rates of reaction with
hydroxyl radicals are quite rapid. However, the chemistry involving
hydroxyl radicals is quite complex in that there are several reactions
involved in their formation as well as reactions between themselves and
reactions involving other radicals or non-organic species in solution.
All of these factors, as well as variations in ozone and uv light levels,
and mixing, make it difficult to project actual process times, based on
literature data, for various hazardous wastes in the HWWTS.
Consequently, the literature data alone cannot be used to estimate
process times in the HWWTS. However, these data can be used to determine

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whether treatment of specific hazardous wastes in the HWWTS is feasible in terms of reasonable process times and innocuous reaction products.

2. Experimental Apparatus

Figure 1 is a block diagram of the experimental apparatus used in these studies. The sample to be studied, an aqueous solution typically containing 200 ppm of the compound of interest, is contained in the reactor. The reactor is a heavy glass wall container sealed with stainless steel end plates. Tank oxygen flows through an ozone generator, and the resulting ozone/oxygen mixture passes into the reactor, where it bubbles through the aqueous solution from twelve 0.040 in. holes pointing downward. The gas mixture passes out of the reactor, through a gas line containing detachable traps, and into a backup vessel containing either water or an alkaline sulfite mixture capable of destroying unreacted ozone. Gas coming out of the backup vessel passes through an ozone destruct trap containing molecular sieve and then into a separately vented hood. Other gas lines shown in the Fig. 1 allow for ozone measurement before and after flow through the reactor.

Also shown in Fig. 1 is a 6 W uv lamp immersed in a quartz tube in the reactor that transmits 254 nm uv light. The reactor is equipped with a sample port that can also be used to inject water to make up that lost by evaporation. The reactor contains an anvil (shown in the top right portion of the reactor, immersed in solution) capable of holding metal coupon samples, to monitor for corrosion.

The traps can be used to condense volatiles coming out of the reactor. Trap temperatures are kept at or above dry ice temperature so as not to condense ozone. Ozone can be explosive in condensed form. Alternatively, evaporative losses are measured by bubbling nitrogen through the reactor containing the material of interest (as well as potential reaction products). Analysis of samples from the reactor before and after nitrogen bubbling yields the evaporative losses.

The purpose of these experiments was to determine the process time required to treat each material and the completeness of the treatment. Information from the literature provided some guidelines, at least for treatment of the parent compound. Some trial and error was required to determine process time required to fully treat all intermediate
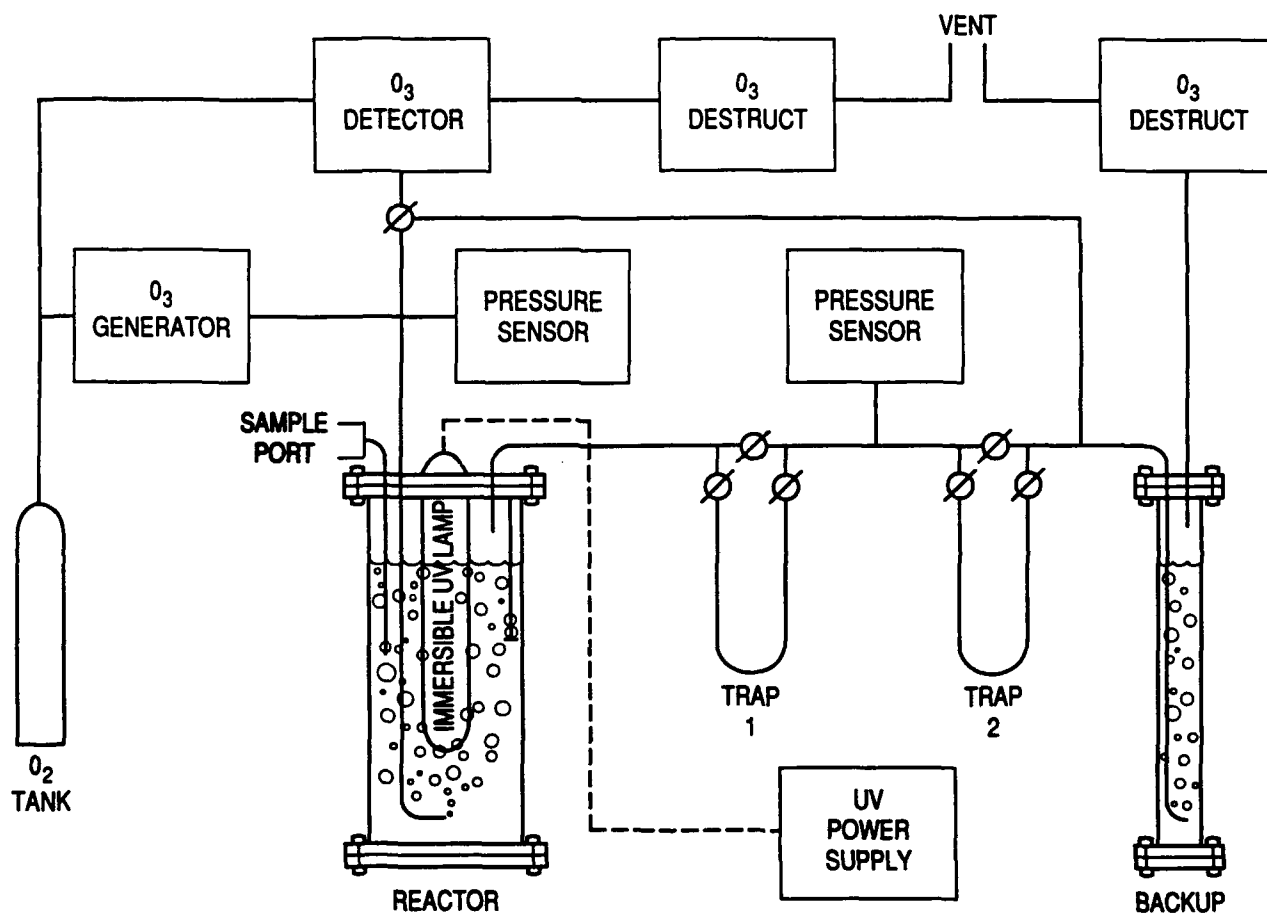
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Figure 1. Experimental apparatus.

compounds.

The progress of the treatment was monitored by analysis of reactants and products as a function of treatment time. This was done using gas chromatography (GC) with flame ionization detection. [The chromatograph was a Hewlett-Packard model 5840A, using a glass capillary column from J&W Scientific (DB Wax, 30 m x 0.32 mm I.D., P/N 123-7033). Detection sensitivity was generally about 0.5 to 1 ppm for most of the starting materials studied here, except for the chlorinated compounds, which had detection sensitivities of 2 to 3 ppm.] The emphasis of the analyses was to monitor the disappearance of the parent compounds and the appearance and eventual disappearance of intermediates. Where possible, based on anticipated reaction products, intermediates were identified. Of particular interest was comparison of the gas chromatograms of the (high purity) water before addition of the parent compound, after addition, and after treatment. Of course, the ideal situation was where the chromatogram of the treated solution was identical to that of the water before addition of the parent compound. In the case of the chlorinated hydrocarbons, separate analyses were carried out for inorganic chloride in solution, using a chloride specific ion electrode.

3. <u>Extrapolation of Laboratory Results to the HWWTS</u>

As will be seen in the discussion below, attack by hydroxyl radicals will probably be the most important reaction in most cases. The hydroxyl radicals result from photolysis of ozone and subsequent reactions of the oxygen sing'et D atom formed with water (refs. 2,3). The number of hydroxyl radicals produced in a system will depend on the ozone injection rate and the amount of uv light in the system. If the number of ozone molecules injected per unit time is greater than the number of photons produced in that same time, then the photon generation rate will control the rate of hydroxyl radical production. [Each photon absorbed will result in the destruction of one ozone molecule and in the ultimate production of two hydroxyl radicals (refs. 2,3,6)]. Conversely, if the number of photons generated per unit time exceeds the rate of injection of ozone molecules, then this rate will govern the rate of hydroxyl radical production.

We would expect the treatment time required to destroy a particular hazardous waste, plus its intermediate oxidation products, to be

inversely proportional to the hydroxyl radical concentration or the rate of production. The rate of production would be equal to the rate of ozone injection or uv photon production, whichever is the limiting rate. Similarly, the treatment time should be proportional to the total amount of hazardous waste to be treated, i.e., the product of the concentration and volume of waste. We will use these simple principles to extrapolate our experimental results to the HWWTS in order to estimate times that will be required in the field to treat various hazardous wastes.

As an example, consider the case of ozone/uv treatment of acetic acid, for which a great deal of experimental data exist (refs. 7-10). Figure 2 plots the rates of destruction of acetic acid and its intermediate oxidation products in terms of total organic carbon (TOC) versus treatment time. Table 1 lists experimental parameters from the experiments discussed in refs. 7-10, along with parameters from our experimental apparatus and the HWWTS. Note that in all cases, low pressure mercury lamps were used with the major uv output at 254 nm. The uv output was estimated by using the lamp wattage and assuming a 20% conversion to photons, which is typical of low pressure mercury lamps (ref. 6). In the case of the HWWTS lamps, the uv output given in the manufacturer's specifications after 100 hr of lamp operation was used (ref. 11).

From Table 1, it will be seen that the hydroxyl radical production rate would be limited by the photon generation rate in refs. 8 and 9, as well as in our study here and in the HWWTS. In refs. 7 and 10, the hydroxyl radical production rate would be limited by the ozone injection rate. In each case, dividing the total moles of acetic acid by the limiting rate (here and in the HWWTS, we assume a concentration of 100 ppm or 1.67 mmoles/l), and using a single normalization factor for all experiments, the approximate treatment time can be estimated to reduce the TOC to some specified value. For the first four experiments listed in Table 1, we estimate treatment times required to reduce the TOC to 1/2 as 33, 49, 159, and 53 min, respectively, compared to measured values of 84, 45, 158, and 47 min. Note that except for the experiment in ref. 7 (where there is a discrepancy of about a factor of 2 1/2), the estimated and measured half-lives are in excellent agreement. (Examination of the literature for these four experiments suggests the
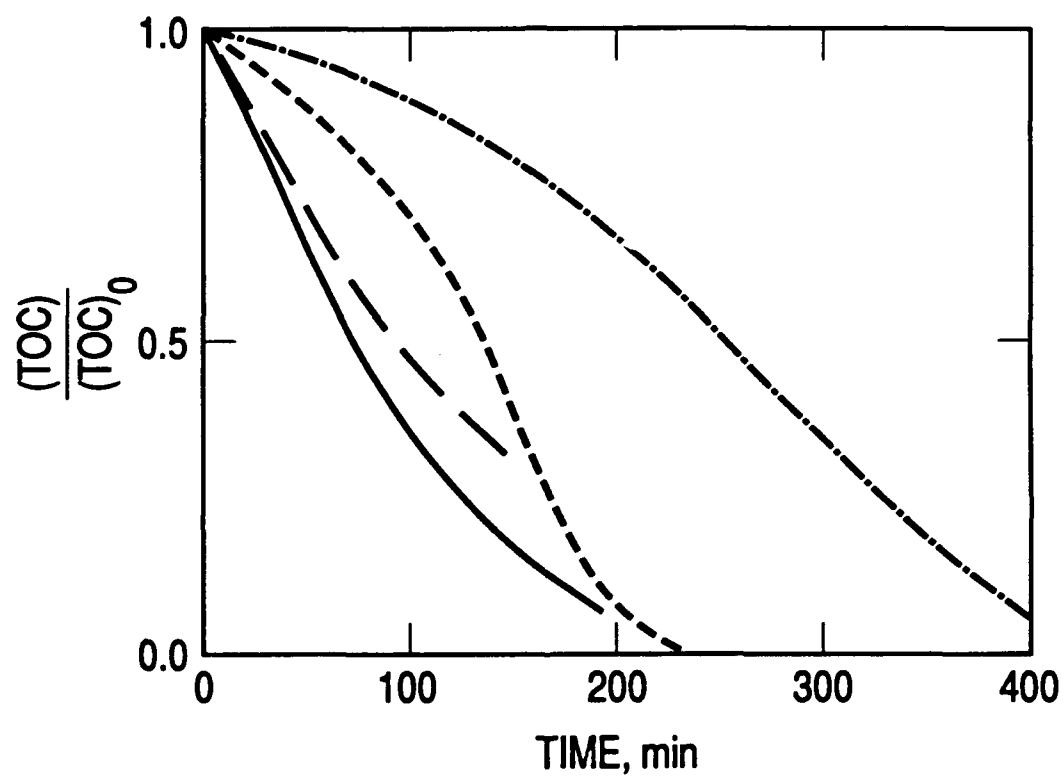
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Figure 2. Total organic carbon decay in the ozone/uv treatment of acetic acid. Short-dashed curve, ref. 7; solid curve, ref. 8; long- and short-dashed curve, ref. 9; long-dashed curve, ref. 10.

Table 1. Parameters for Various Acetic Acid Experiments.

Ref.	Ozone Injection (mmole/hr)	Photon Generation (mEinstein/hr)[a]	Volume (l)	Concentration (mmole/l)	Total Acid (mmole)
7	97.5	178.1	10	1.60	16.0
8	125.0	22.3	4	1.33	5.3
9	55.6	22.3	9.92	1.75	17.4
10	16.5	74.2	3	1.42	4.3
Here[b]	57.6	8.9	2.8	1.67	4.7[d]
HWWTS[c]	61,200	24,500	8,330	1.67	13,900[d]

[a] 1 mEinstein/hr = 6.02×10^{20} photons/hr.

[b] For an oxygen flow rate of 3 l/min with 1.2% (weight) of ozone.

[c] For an oxygen flow rate of 30 cfm with 4.5% (weight) of ozone.

[d] Although experiments were not carried out at Aerospace and in the HWWTS with acetic acid, these figures represent the total amount of acid that would be present if 100 ppm solutions were to be treated.

discrepancy in ref. 7 may be due to a mixing problem.) For comparison, the estimated half-lives for treatment of acetic acid in our laboratory (this experiment was not actually be carried out) and in the HWWTS are 106 and 116 min, respectively.

The method outlined here for estimating treatment times from our laboratory results for the various hazardous wastes of interest in the HWWTS will be similar to the method described above for the acetic acid example.

B. Treatment of Specific Wastes

   1. Methyl Alcohol

     a. Literature Results

A number of studies have focused on the ozone treatment of methyl alcohol wastes (refs. 4,7,12-16) and on ozone treatment of products formed from the ozonolysis of methyl alcohol (refs. 5,17-20). It seems fairly well established that initial ozonolysis converts methyl alcohol to formaldehyde. Continued ozonolysis converts the formaldehyde to formic acid, which, in turn, is ultimately converted to carbon dioxide and water (refs. 12,14,17).

Direct attack of ozone on methyl alcohol is a slow process exhibiting a second order rate constant of 0.02 l/mole-sec (refs. 4,15,16). For the conditions of interest in the HWWTS, the Henry's law equilibrium concentration of ozone in solution would be about 1×10^{-4} moles/l (ref. 21). Under these conditions, the methyl alcohol would be destroyed by direct ozone attack with a half-life of 4 days. On the other hand, reaction of methyl alcohol with hydroxyl radicals (produced from ozone in the HWWTS by uv light) occurs with a second order rate constant over 10 orders of magnitude greater than that for the ozone-methyl alcohol reaction at 5.0×10^{8} l/mole-sec (ref. 22). Consequently, the hydroxyl radical attack on methyl alcohol should be the dominant reaction path in the HWWTS. Of course, the dominance of the hydroxyl radical reaction mandates that the uv in combination with the ozone is required to treat the methyl alcohol in a reasonable time.

Formaldehyde, the initial product in the oxidation of methyl alcohol, also reacts slowly with ozone [second order rate constant of 0.1 l/mole-sec (ref. 16)]. With formaldehyde also, the hydroxyl radical reaction would be the dominant reaction path. In the case of formic

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acid, the oxidation product of formaldehyde, the ozone reaction is faster with the neutral acid, being about 5 l/mole-sec, and even faster with the formate ion, at about 100 l/mole-sec (refs. 4,17-19). Direct ozone reactions with formic acid and the formate ion should contribute to their conversion to carbon dioxide. However, hydroxyl radical reactions should also contribute, since the rate of their reaction with formic acid is 2×10^8 l/mole-sec and with the formate ion is 2×10^9 l/mole-sec (refs. 5,15).

The literature results indicate that the treatment of methyl alcohol by ozone leads, in a relatively straightforward manner, to formaldehyde, formic acid, and, ultimately, carbon dioxide and water. Therefore, methyl alcohol should be readily treatable in the HWWTS. However, since the direct reactions of methyl alcohol (and formaldehyde) with ozone are quite slow, it is imperative that the HWWTS treatment employ both ozone and uv, and not ozone alone. This conclusion is supported by one study that compared the relative efficiencies of treating methyl alcohol by ozone, uv, and ozone/uv (ref. 7). After 3 hr of exposure of methyl alcohol to ozone or uv, destruction of methyl alcohol (and intermediate oxidation products) as measured by TOC analyses indicated that TOC removal was 0 and 7%, respectively. By contrast, TOC removal was 100% after 2 hr of treatment by ozone/uv.

b. Experimental Results

Figure 3 exhibits results from an experiment in which methyl alcohol was treated with ozone/uv in our apparatus. In that experiment, the starting concentration of methyl alcohol was 200 ppm, and the ozone content of the oxygen flow stream was approximately 1.2 wt%. The ozone content of the gas stream effluent from the reactor was virtually the same as the influent concentration (about 1.1%), indicating that the reaction was slow and little ozone was consumed. The pH of the solution at the end of the reaction (a total of 780 min exposure to ozone/uv) was 6.1. A second experiment, conducted over a shorter period of time (120 min), gave results in good agreement with those in Fig. 3. A TOC analysis of a sample after the 780 min exposure indicated a TOC level at the detection limit of 1 ppm (plus or minus 1 ppm). (Note that a pure water blank gave an identical TOC result of 1 ppm, plus or minus 1 ppm.)

In our experiments, only one peak was observed in the gas
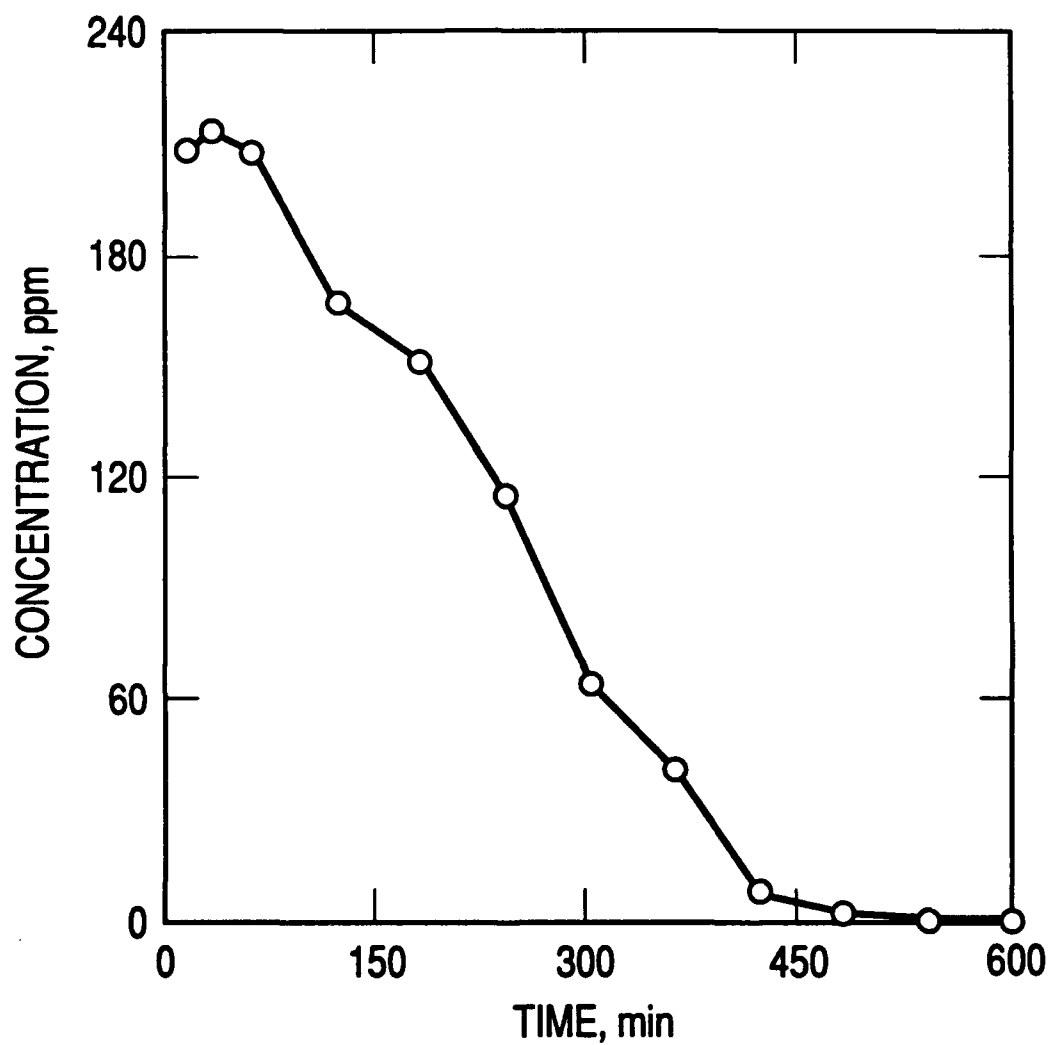
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Figure 3. Ozone/uv treatment of methyl alcohol. Data points are the sum of the methyl alcohol and formaldehyde concentrations unadjusted for sensitivities (see text for discussion).

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chromatograms. However, separate gas chromatograms for methyl alcohol, formaldehyde, and a mixture of the two indicated that these species elute with the same retention time and were not separable with the column and conditions used. Thus, the experimental points in Fig. 3 are likely due to the sum of methyl alcohol and formaldehyde concentrations [the latter species likely to be the initial intermediate in the ozone/uv treatment of methyl alcohol (refs. 5,17-20)]. This is likely the reason for no initial decay in concentration as determined from GC analysis since, although methyl alcohol is being decomposed, formaldehyde is being formed and the sum of the two (neglecting possible slight differences in detection sensitivities) remains approximately constant. With continued treatment, however, the formaldehyde also begins to decompose, along with the methyl alcohol, so that the single gas chromatographic peak observed does decrease. We estimate detection limits for methyl alcohol and formaldehyde of about 1 ppm. A separate experiment in which nitrogen was bubbled through the reactor at 3 1/min indicated a minimal evaporation rate of 3.0%/hr for methyl alcohol. [Assuming equilibrium is established between the aqueous and gas phases, the Henry's Law constant can be estimated for methyl alcohol in water from the evaporation rate. The value obtained is 0.60 atm/mole fraction, which is in reasonable agreement with the value of 0.26 atm/mole fraction calculated from thermodynamic data available in the literature (ref. 23), considering the limits of the experiment here.]

Based on literature data (ref. 7) relative to ozone/uv treatment of methyl alcohol, and likely intermediate products of ozone/uv treatment of methyl alcohol, such as formaldehyde and formic acid, we anticipate that TOC would be reduced to less than 1 ppm after approximately 10-13 hr of treatment. Using these values and extrapolating our results (and those in ref. 7) in the manner outlined in section II.A.3., we find that treatment of a 100 ppm solution of methyl alcohol in the HWWTS would require about 7 to 13 hr to reduce the TOC in the HWWTS to less than 1 ppm.

The data obtained here and in the literature indicate that methyl alcohol should be quite capable of being treated by ozone/uv in the HWWTS. The estimated treatment time to reduce the TOC to less than 1 ppm should be of the order of 7 to 13 hr.

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2. Isopropyl Alcohol

a. Literature Results

In contrast to methyl alcohol, direct reaction of ozone with isopropyl alcohol occurs at a much faster rate, with a half-life of approximately 1 hr (refs. 4,15,16). As in the case of methyl alcohol, the hydroxyl reactions are expected to be fast. Although the hydroxyl reaction path may dominate, direct ozone reactions are likely to contribute to the destruction of isopropyl alcohol.

The initial product of ozonolysis of isopropyl alcohol appears to be acetone in almost quantitative yield (refs. 8,12). Small amounts of formaldehyde and acetic acid are also formed (ref. 12). The direct reaction of ozone with acetone is slow, with a second order rate constant of 0.032 1/mole–sec (ref. 16). However, ozone/uv treatment (including hydroxyl radical attack) is reasonably rapid and produces formaldehyde and a mixture of organic acids, including formic, acetic, and oxalic acids (ref. 8,24). The acids are attacked slowly by direct ozone reactions (refs. 7,8,15) but reasonably rapidly by hydroxyl radicals produced in the presence of ozone/uv (refs. 4,7–9,15,20). These final steps are likely to lead to the production of carbon dioxide and water.

Here, as in the case of methyl alcohol, ozone/uv treatment in the HWWTS should be capable of treating isopropyl alcohol reasonably rapidly, with the ultimate formation of innocuous end products. The literature data (ref. 8) for isopropyl alcohol (also known as 2-propanol) show very clearly the advantages of ozone/uv treatment over ozone treatment alone, as illustrated in Fig. 4. The top and bottom graphs in that figure compare ozone and ozone/uv treatment for identical experimental conditions, except for the uv light. It can be seen from those graphs that ozone/uv destroys the isopropyl alcohol in 45 min, while ozone alone requires 105 min. Moreover, acetone, which is the major oxidation product, reaches a peak concentration in 105 min in the ozone–only treatment and is destroyed slowly after that amount of time. This result contrasts to the results for the ozone/uv treatment, where the acetone is totally destroyed in 75 min. In addition, TOC exhibits only a 17% decrease after 2 hr of ozone–only treatment, while ozone/uv leads to an 82% reduction for the same treatment time and a 90% reduction after 2.25 hr of treatment.
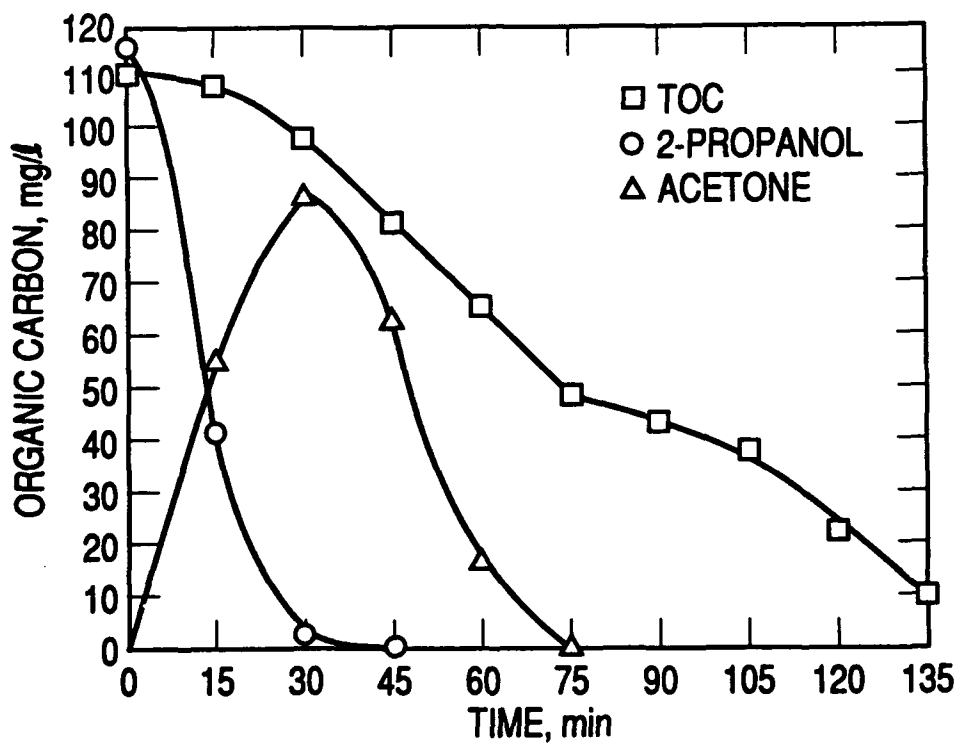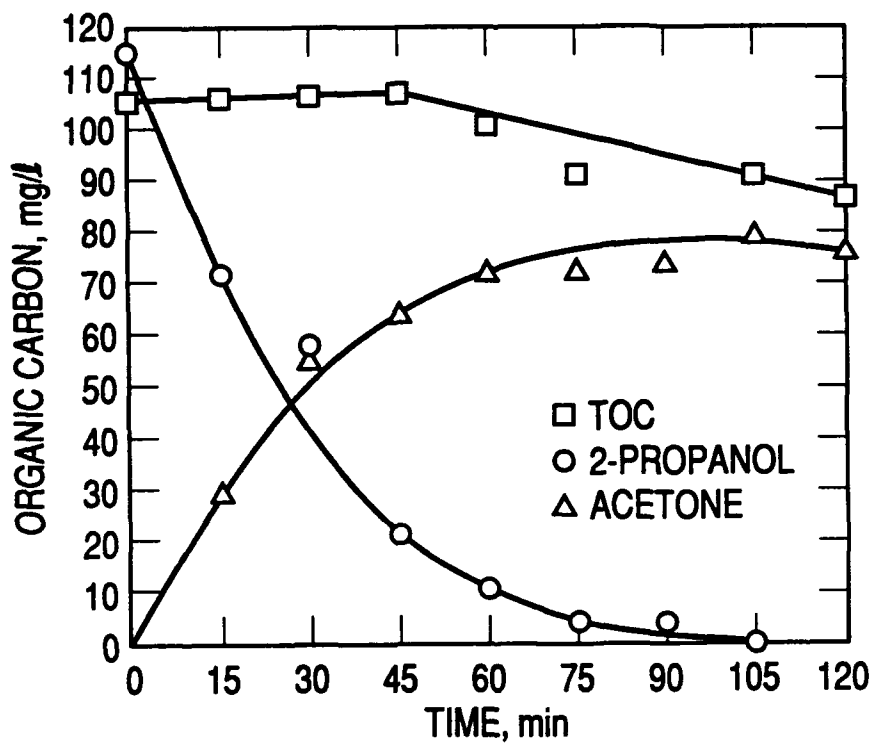
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Figure 4. Ozone (top) and ozone/uv (bottom) treatment of isopropyl alcohol.

b. Experimental Results

Figure 5 exhibits results from an experiment in which isopropyl alcohol was treated with ozone/uv in our system. In that experiment, the starting concentration of isopropyl alcohol was 200 ppm and the ozone content of the oxygen flow stream was approximately 1.1 wt%. Note that the ozone content of the gas stream effluent from the reactor was virtually the same as the influent concentration, indicating that the reaction is slow and little ozone is consumed. The pH of the solution at the end of the reaction (540 min) was 3.7. A second experiment, conducted over a shorter period of time (120 min), gave results in good agreement with those in Fig. 5.

Note that in our experiments, no species other than isopropyl alcohol and acetone were detected (detection limits for these two compounds were about 1 ppm). Acetic acid standards indicated the GC peak for acetic acid was broad and could only be detected at concentrations exceeding about 30 ppm. A separate experiment in which nitrogen was bubbled through the reactor at 3 l/min indicated a minimal evaporation rate for isopropyl alcohol of 3.9%/hr, while acetone evaporated at the rate of 9.6%/hr. (These rates translate to values of 0.78 and 2.1 atm/mole fraction estimated for the Henry's Law constants for isopropyl alcohol and acetone in water, respectively.)

Note that the data in Fig. 5 for isopropyl alcohol and acetone are strikingly similar, except for the time scale, to the data in Fig. 4 [bottom graph (ref. 8)]. The shorter time scales for the data in Fig. 4 are likely due to the lower initial concentration of isopropyl alcohol being treated, as well as to the higer ozone and uv outputs used in those experiments.

Extrapolation of our results (and those in ref. 8) in the manner outlined in section II.A.3. indicates that treatment of a 100 ppm solution of isopropyl alcohol in the HWWTS would require about 1 to 1.5 hr to reduce the alcohol concentration to less than 1 ppm. Similarly, projected time to reduce both the alcohol and acetone concentration to less than 1 ppm would be about 2 to 4.5 hr. Assuming, as was observed in ref. 8, that the time required to reduce the TOC to less than 1 ppm is approximately twice that required to reduce the isopropyl and acetone concentrations to those levels, the projected time required to reduce the
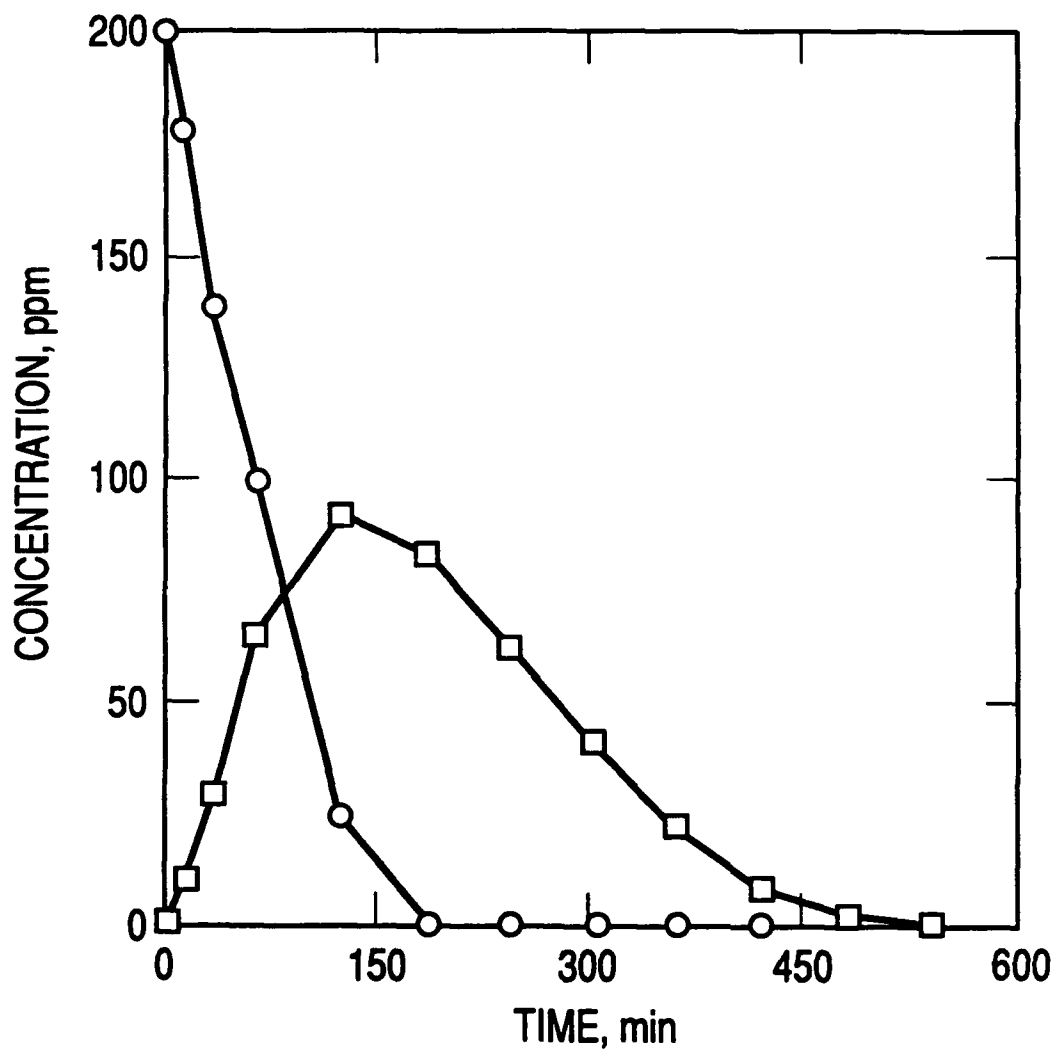
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Figure 5. Ozone/uv treatment of isopropyl alcohol. Open circles represent the isopropyl alcohol concentration as a function of time. Open squares are the acetone concentration (produced from oxidation of isopropyl alcohol) as a function of time.

TOC in the HWWTS to less than 1 ppm is estimated to be 4-9 hr.

The data obtained from our experiments and in the literature indicate that isopropyl alcohol should be quite capable of being treated by ozone/uv in the HWWTS. The estimated treatment time to reduce the TOC to less than 1 ppm should be of the order of 4 to 9 nr.

3. Trichloroethylene

a. Literature Results

Ozone attack on trichloroethylene occurs with a second order rate constant of 17 l/mole-sec in aqueous solution (refs. 4,15,16,25), although the rate in carbon tetrachloride solution is about a factor of 5 lower (ref. 26). The aqueous ozone rates indicate a half-life of about 6 min for direct ozone attack on trichloroethylene in the HWWTS. The rate of hydroxyl radical attack is fast (refs. 4,5,15,25) and likely will dominate trichloroethylene decomposition in the HWWTS. In the presence of ozone and uv, the rate of trichloroethylene decomposition can increase by up to a factor of 20 or more over that of ozone induced decomposition alone (ref. 27). Note that for the chlorinated ethylenes, the rate of direct ozone attack is very dependent on the degree of chlorination. For tetrachloroethylene, the second order rate constant for the aqueous phase ozone attack is <0.1 l/mole-sec (refs. 4,15,16). Conversely, the rate constants for the dichloroethylenes are 1-3 orders of magnitude greater than the rate constant for trichloroethylene (refs. 4,15,16,26), while the rate constants for monochloroethylene (vinyl chloride) and ethylene itself are even higher (ref. 26).

The only literature data found on reaction products were for ozonolysis of dichloroethylenes and vinyl chloride in carbon tetrachloride solution (ref. 26). (Ozonolysis of trichloroethylene should yield similar products.) These data suggest that the main reaction is destruction of the double bond and splitting of the molecule to form one carbon oxychlorides. The carbon oxychlorides would rapidly hydrolyze in aqueous solution to form hydrochloric acid, carbon dioxide, and possibly small amounts of formic acid. For starting concentrations of 100 ppm of trichloroethylene, up to 83 ppm of hydrochloric acid could be generated. It is anticipated that these concentrations, resulting from infrequent treatments of chlorinated hydrocarbon wastes, should not lead to any corrosion. Previous tests with immersion of stainless steels

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in pH 1-5 nitric acid containing 100 ppm of chloride for 7 to 11 days produced no evidence of corrosion (ref. 28). Chloride corrosion in the form of pitting or crevice corrosion would be expected more in a stagnant, oxygen depleted system (ref. 29), as opposed to a gas mixed, water recirculated, oxygen/ozone-rich system in the HWWTS.

   b. Experimental Results

An initial experiment conducted with trichloroethylene under conditions similar to those used for the methyl and isopropyl alcohol experiments (oxygen/ozone flow rate of 3 l/min and an ozone concentration of 1.1 to 1.2%) indicated a very high evaporation rate. Consequently, the flow rate was reduced (to 0.3 l/min) to reduce evaporation. This led to an increase in the ozone concentration in the gas stream to approximately 2% (ozone could not be accurately measured at flow rates below 1 l/min).

Figure 6 exhibits results from two separate experiments in which trichloroethylene was treated with ozone/uv. The decay rate is somewhat faster than that observed for isopropyl alcohol, suggesting contributions of direct ozone attack on the trichloroethylene. Indeed, some supporting evidence for this conclusion comes from sample analyses. Samples were generally analyzed by GC within a few minutes after removal from the reactor. However, samples were not purged of residual ozone before analysis. This led to a slight decay of the GC peaks with time, indicating that the residual ozone was reacting with the trichloroethylene in the sample vials (small corrections to the data were made for these effects). However, increased ozone concentrations in the reactor and higher evaporation rates (even at the lower overall flow rates used in the trichloroethylene experiments) also contributed to the faster decay rates observed here, relative to isopropyl alcohol. Indeed, the evaporation rate for the trichloroethylene (1.8%/min) accounted for about 40% of the trichloroethylene loss, with chemical degradation accounting for the remaining 60%. (These percentages were estimated by fitting the decay curves approximately by exponential functions. The resulting exponential decay constants yield the evaporative rate loss and, in the ozone/uv experiment, the reactive+evaporative rate loss.) The evaporation rate measured for the trichloroethylene equates to a Henry's Law constant of 210 atm/mole fraction. A TOC analysis after
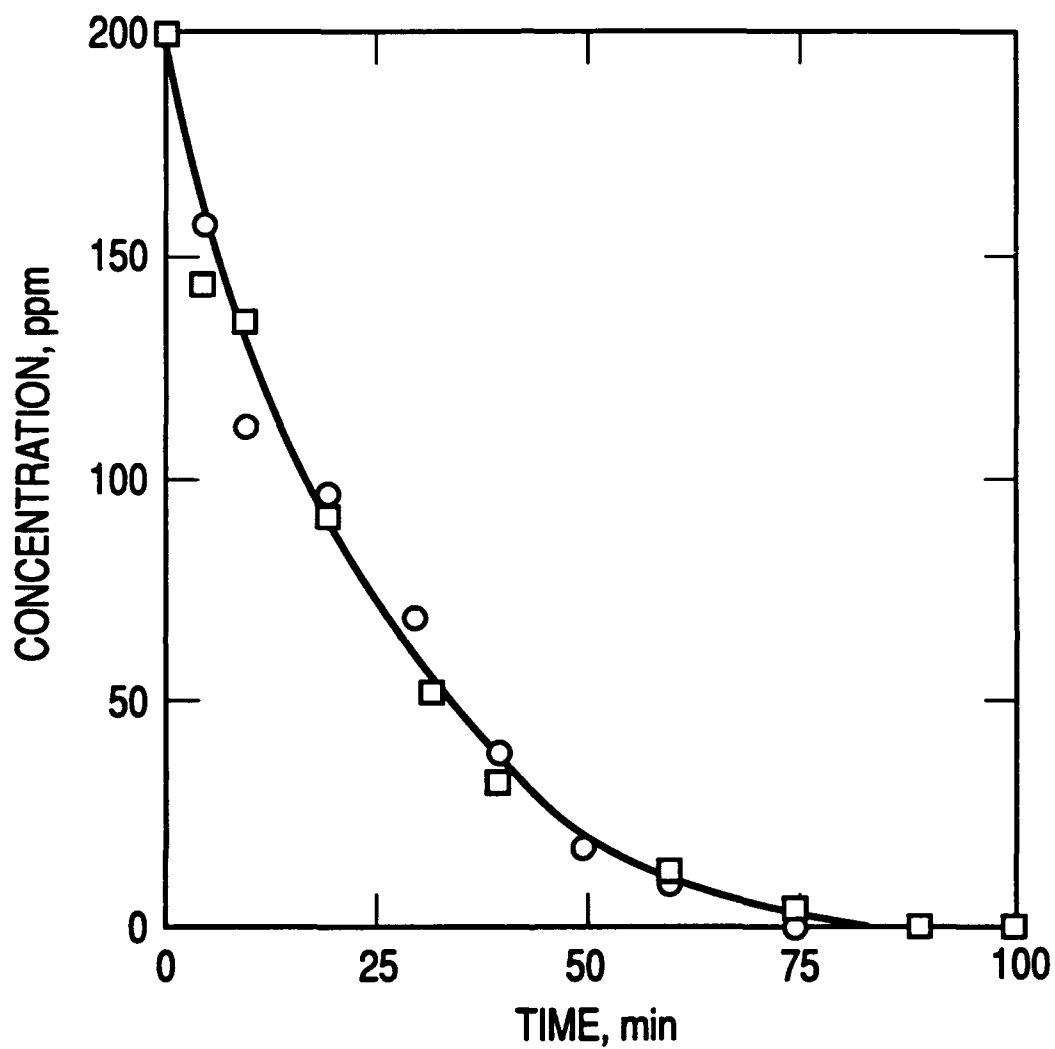
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Figure 6. Ozone/uv treatment of trichloroethylene. Open circles and
squares are data from two separate experiments.

approximately 3 hr exposure to ozone/uv indicated a level of 2 ppm, relative to a detection limit of 1 ppm, plus or minus 1 ppm.

The pHs at the end of the experiments (total ozone/uv exposure of about 3 hr) were 2.9 and 3.1, most likely due to the formation of hydrochloric acid. If all of the trichloroethylene were converted to HCl and that HCl remained dissolved in solution, one would expect a pH of 2.3. The difference in the calculated and observed pHs indicates possibly the formation of some chlorinated intermediates (not detectable by GC) that were not completely decomposed in the 3 hr treatment, or some evaporative losses of the parent trichloroethylene or product HCl. Measured chloride ion concentrations (chloride specific ion electrode) were 2.8×10^{-3} and 2.0×10^{-3} M, respectively, compared to anticipated concentrations of 4.6×10^{-3} M if the trichloroethylene were quantitatively converted to HCl in solution. Inspection and weighing of 316L stainless steel and tungsten samples put into the reactor during these experiments indicated, as anticipated, no corrosion losses.

Extrapolation of these results in the manner outlined above indicates that a 100 ppm solution of trichloroethylene could be reduced to <1 ppm in the HWWTS in about 52 min. Of course, other intermediate compounds may be formed during treatment, for instance, possibly formic acid. Allowing for these, full treatment of 100 ppm solutions of trichloroethylene in the HWWTS should not require more than 2-3 hr to reduce all organic residues to less than 1 ppm.

4. 1,1,1-Trichloroethane

a. Literature Results

The only literature data found on the reaction between ozone and 1,1,1-trichloroethane indicates this reaction is about a factor of 170 slower than the ozone-trichloroethylene reaction, with a second order rate constant of about 0.1 1/mole-sec (ref. 30). This value is consistent with other values for chlorinated methanes (refs. 16,25) or other unchlorinated hydrocarbons (refs. 25,31), which are generally <0.1 1/mole-sec, although one study does find a value of 4.3 1/mole-sec for the reaction of ozone with 1,2-dichloroethane (ref. 27). As with the other materials investigated, the rate constants for the hydroxyl reactions are much faster than those for the ozone reactions, although they appear to be a factor of 10 to 100 lower than the rate constant for

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the hydroxyl radical reactions with methyl or isopropyl alcohols (refs. 4,15,25). Consequently, we might expect the hydroxyl radical reactions to dominate here, although overall reaction rates may be somewhat slower than those for the alcohols.

Little information is available in the literature concerning reaction products. However, we might expect carbon-carbon bond cleavage to produce chlorinated methanes and methyl alcohol, or oxidation products of these species. Alternatively, or in addition, the methyl group in the 1,1,1-trichloroethane might be oxidized sequentially to the alcohol, aldehyde, and acid. These various intermediates should ultimately undergo oxidation and hydrolysis to yield carbon dioxide, water, and hydrochloric acid, provided the intermediates do not volatilize from the solution before they are oxidized. As noted above for trichloroethylene, corrosion by low levels of hydrochloric acid should not be a problem in the HWWTS.

In light of the discussions above, we expect that oxidation of 1,1,1-trichloroethane in the HWWTS will occur at an overall rate comparable to or slower than that for methyl alcohol, with the ultimate production of reaction products that are innocuous and present little health or corrosion problems.

b. Experimental Results

Experiments for 1,1,1-trichloroethane were carried out at 0.3 l/min of oxygen flow with 2 wt% of ozone to minimize evaporative losses. Figure 7 exhibits results from two separate experiments in which 1,1,1-trichloroethane was treated with ozone/uv. The decay rates are slower than those observed for the trichloroethylene but comparable to those seen for isopropyl alcohol. Evaporation losses measured for the 1,1,1-trichloroethane were 0.8%/min, corresponding to a Henry's Law constant of 100 atm/mole fraction. Calculations carried out in the manner described for trichloroethylene indicate that the evaporative losses for 1,1,1-trichloroethane were about equal to losses from chemical decomposition in these experiments.

Measured pHs at the end of the experiments (total exposure to ozone/uv of 2.5 and 3 hr) were 3.7 and 3.3, respectively. Conversion of all of the chlorine in 1,1,1-trichloroethane to dissolved chloride ions (HCl) would result in a pH of 2.3. Here, as in the case of the
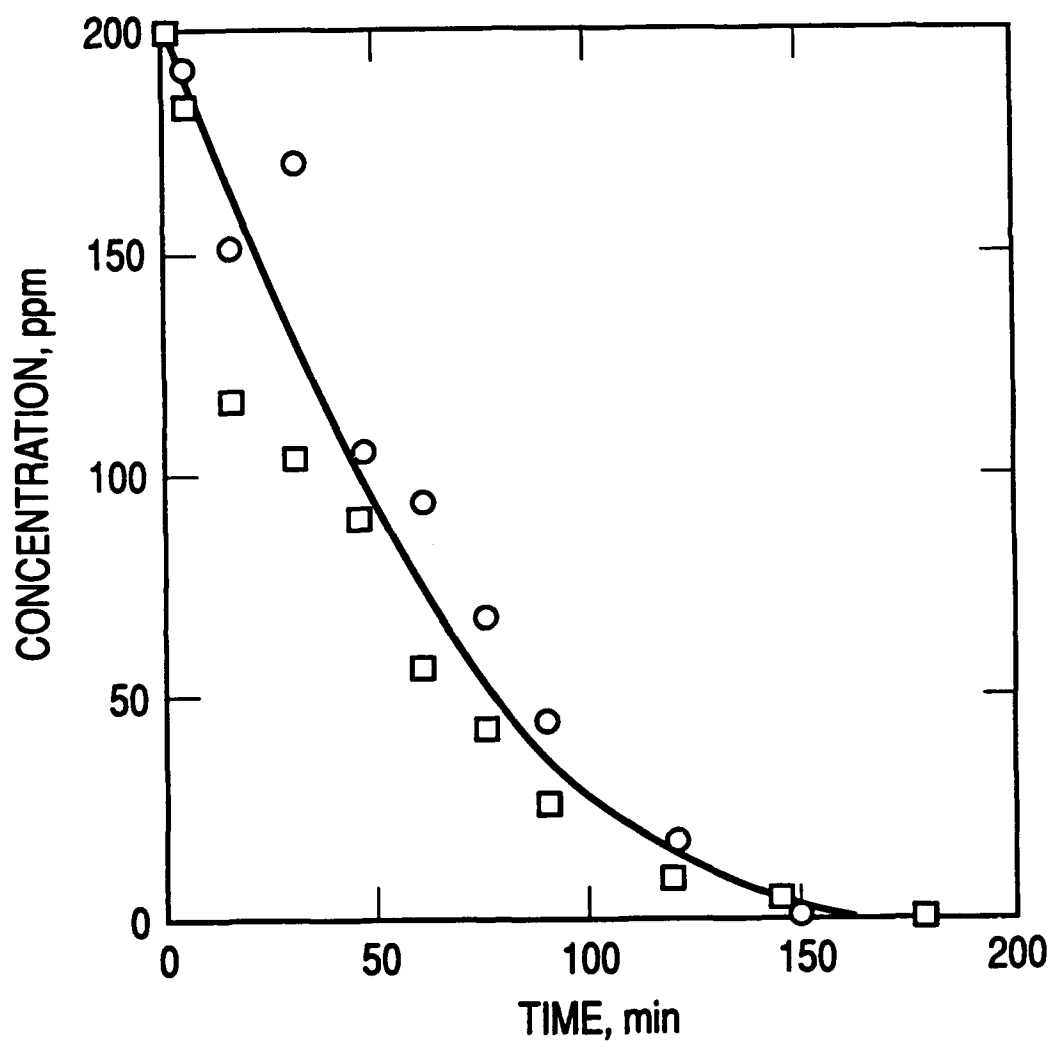
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Figure 7. Ozone/uv treatment of 1,1,1-trichloroethane. Open circles and squares are data from two separate experiments.

trichloroethylene, the discrepancy between the calculated and observed pHs could be due to (undetected) chlorinated organic intermediates that were not completely decomposed during the treatment time or to some evaporative losses of parent 1,1,1-trichloroethane or product HCl. Chloride measurements in solution (specific ion electrode) indicated a concentration of 3.3×10^{-4} M (2.5 hr ozone/uv exposure) compared to a value of 4.5×10^{-3} M expected for quantitative conversion of 1,1,1-trichloroethane to disolved chloride. A TOC analysis of a sample after 2.5 hr exposure to ozone/uv indicated a value at the detection limit of 1 ppm, plus or minus 1 ppm. Measurement (weight) and inspections of 316L stainless steel and tungsten samples before and after the experiments indicated, as expected, no evidence of corrosion.

Projections, based on the experimental results obtained here, and made in the manner described above, indicate that a 100 ppm solution of 1,1,1-trichloroethane can be treated in the HWWTS to less than 1 ppm in about 1 3/4 hr or, allowing for complete destruction of intermediates not detected in the GCs here, in 3 to 5 hr.

5. Benzene

   a. Literature Results

Reactions of benzene with ozone occur with a second order rate constant of 2 l/mole-sec in aqueous solution (refs. 4,15,16,18,20,30) and 0.03-0.09 l/mole-sec in non-aqueous solutions (refs. 13,26,32,33). Rate constants for hydroxyl radical reactions with benzene, reactions that are likely to dominate in the HWWTS, are $5-8 \times 10^9$ l/mole-sec (refs. 4,5,13,15).

Several studies have been carried out on the products of the ozone-benzene reaction in non-aqueous (refs. 32-34) and aqueous (refs. 4,24,33) solutions. The reactions are somewhat similar in that glyoxal and glyoxylic acid are the major intermediate products. In non-aqueous media, other major intermediates are formed that are called peroxidic species, possibly triozonides (refs. 32-34). These species appear to be rapidly hydrolyzed in aqueous media to form the other products that are observed in water solutions (ref. 33). The glyoxal is likely to be converted to glyoxylic acid on continued ozonolysis. The glyoxylic acid is attacked by ozone with a second order rate constant of 0.2 l/mole-sec for the neutral acid and 2 l/mole-sec for the ionized acid

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(refs. 19,20). Continued ozonolysis can produce formic acid and, ultimately, carbon dioxide and water (ref. 33).

The limited data found in the literature (ref. 4) indicate that in addition to the above types of reaction products, reactions of benzene with hydroxyl radicals can lead to radical addition to the benzene ring and to the possible formation of phenols. The addition compounds and phenols are rapidly attacked by ozone (refs. 4,15,16,18,24,35,36) and hydroxyl radicals (refs. 4,15) to form similar types of reaction products as those noted above for ozone reactions with benzene. In addition, small amounts of catechol and hydroquinone are formed from oxidation of phenol (refs. 36-39), which are rapidly converted to non-aromatic reaction products similar to those noted above.

In summary, benzene will be attacked by both ozone and hydroxyl radicals in the HWWTS (the hydroxyl radical reactions likely dominating) to yield a wide variety of intermediate oxidation products. However, all of these products should be ultimately oxidized to innocuous products in a reasonable time in the HWWTS, so that benzene-containing solutions should be readily treatable.

b. Experimental Results

As with the trichloroethylene and 1,1,1-trichloroethane, experiments for benzene were carried out at low flow rates (0.3 l/min) and high ozone concentrations (about 2%) to reduce the loss of benzene due to evaporation. Figure 8 exhibits results from two separate experiments in which benzene was treated with ozone/uv. The decay rates are comparable to those seen for 1,1,1-trichloroethane (compare Figs. 7 and 8). Evaporation losses measured for the benzene were 1%/min, corresponding to a Henry's Law constant of 120 atm/mole fraction. Calculations carried out in the manner described for the chlorinated hydrocarbons indicate that the evaporative losses for benzene were about equal to losses from chemical decomposition in these experiments.

In the two experiments, the benzene concentrations were reduced to below the detection limit (less than 0.05 ppm) in 190 and 160 min, respectively. However, in the former experiment, the ozone/uv treatment was continued for 280 min, and a sample was taken for TOC analysis (analysis indicated a TOC of 17 ppm after 280 min). Measured pHs at the end of these experiments were both 3.5.
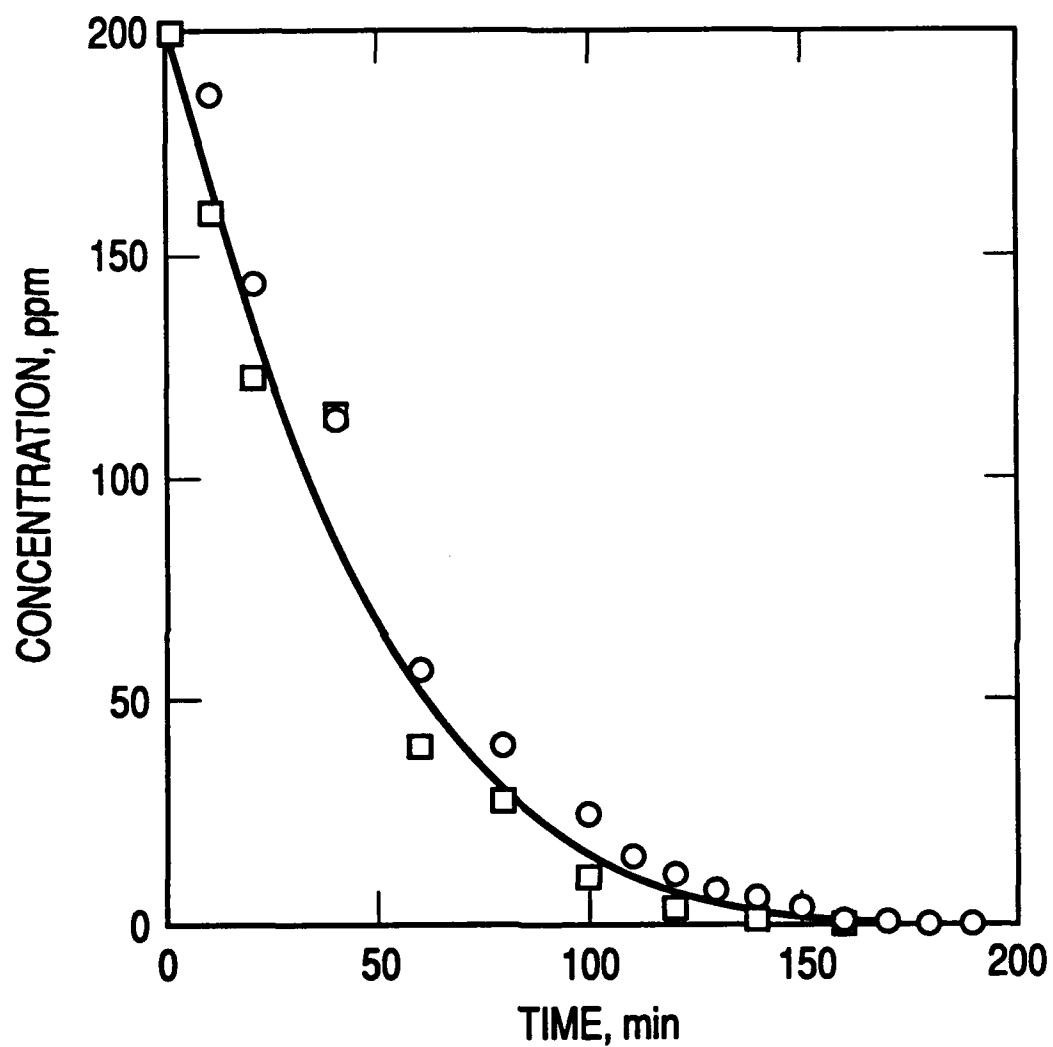
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Figure 8. Ozone/uv treatment of benzene. Open circles and squares
are data from two separate experiments.

Projections, based on the experimental results obtained here, and made in the manner described above, indicate that a 100 ppm solution of benzene can be treated in the HWWTS to less than 1 ppm in about 1 3/4 hr or, allowing for complete destruction of intermediates not detected in the GCs here, in 3 to 5 hr.

6. Substituted Benzenes

a. Literature Results

The second order rate constant for ozone attack on toluene is 14 l/mole-sec (refs. 4,15,16), while the rate constants for attack on the xylenes are 90-140 l/mole-sec (refs. 4,15,16,18,20), and those for attack on the trimethyl benzenes are 400-700 l/mole-sec (refs. 4,15). Similar trends, increasing the rate of ozone attack with increasing methyl (or ethyl or isopropyl) substitution on the benzene rings, are also observed for non-aqueous solutions. These trends continue all the way up to hexamethyl benzene, although absolute rate constants are lower than those observed in aqueous solutions (refs. 32-34). The rate constants for hydroxyl radical attack on toluene, the xylenes, and trimethyl benzenes are all similar, at $6-7 \times 10^9$ l/mole-sec (refs. 4,5,15,20). Although the hydroxyl radical reactions are likely to be most important for toluene in the HWWTS, the direct ozone reactions should increasingly contribute for increasingly (alkyl) substituted benzenes.

The products of the reactions of the substituted benzenes are similar to those of benzene itself, with the appropriate alkyl substituents (refs. 24,32-34). Thus, for example (ref. 34), oxidation of o-xylene yields a mixture of glyoxal, methylglyoxal, and biacetyl reaction products instead of just glyoxal (in addition to other products). Here, as in the case of benzene, these intermediate products should be readily oxidized to innocuous products so that the substituted benzenes should be capable of being treated in the HWWTS within a reasonable time frame.

b. Experimental Results

Experiments for toluene were carried out under the same low flow (0.3 l/min) and high ozone concentrations (about 2%) used in the chlorinated hydrocarbon and benzene experiments. The reason for selection of these operating parameters was the same as in those experiments, namely, high evaporation losses.

Figure 9 exhibits results from two separate experiments in which toluene was treated with ozone/uv. The decay rates are comparable to those seen for 1,1,1-trichloroethane and benzene (compare Fig. 9 with Figs. 7 and 8). Evaporation losses measured for the toluene were 1.2%/min, corresponding to a Henry's Law constant of 140 atm/mole fraction. Calculations carried out in the manner described above indicate that the evaporative losses for toluene were slightly greater than losses from chemical decomposition in these experiments.

In the two experiments, the toluene concentrations were reduced to below the detection limit in about 140 min. In one experiment, the ozone/uv treatment was continued for 270 min (the other experiment was discontinued after 150 min), and a sample was taken for TOC analysis. The TOC analysis indicated a concentration of 7 ppm (plus or minus 1 ppm). Measured pHs at the end of these experiments were 3.4 (270 min ozone/uv exposure) and 3.3 (150 min ozone/uv exposure).

The results indicate that although toluene totally disappears in about 140 min, the TOC has been reduced (from an initial value of 183 ppm) to about 7 ppm after a 270 min exposure to ozone/uv (no other discernible peaks were observed in the gas chromatograms). If it is assumed that the TOC is decaying linearly with time (ozone/uv exposure), an additional 10-15 min would be required to reduce the TOC from the 7 ppm observed after 270 min to less than 1 ppm. Projections carried out in the manner described above, and based on the experimental results, indicate that a 100 ppm solution of toluene can be treated in the HWWTS to less than 1 ppm in about 3-5 hr (TOC less than 1 ppm).
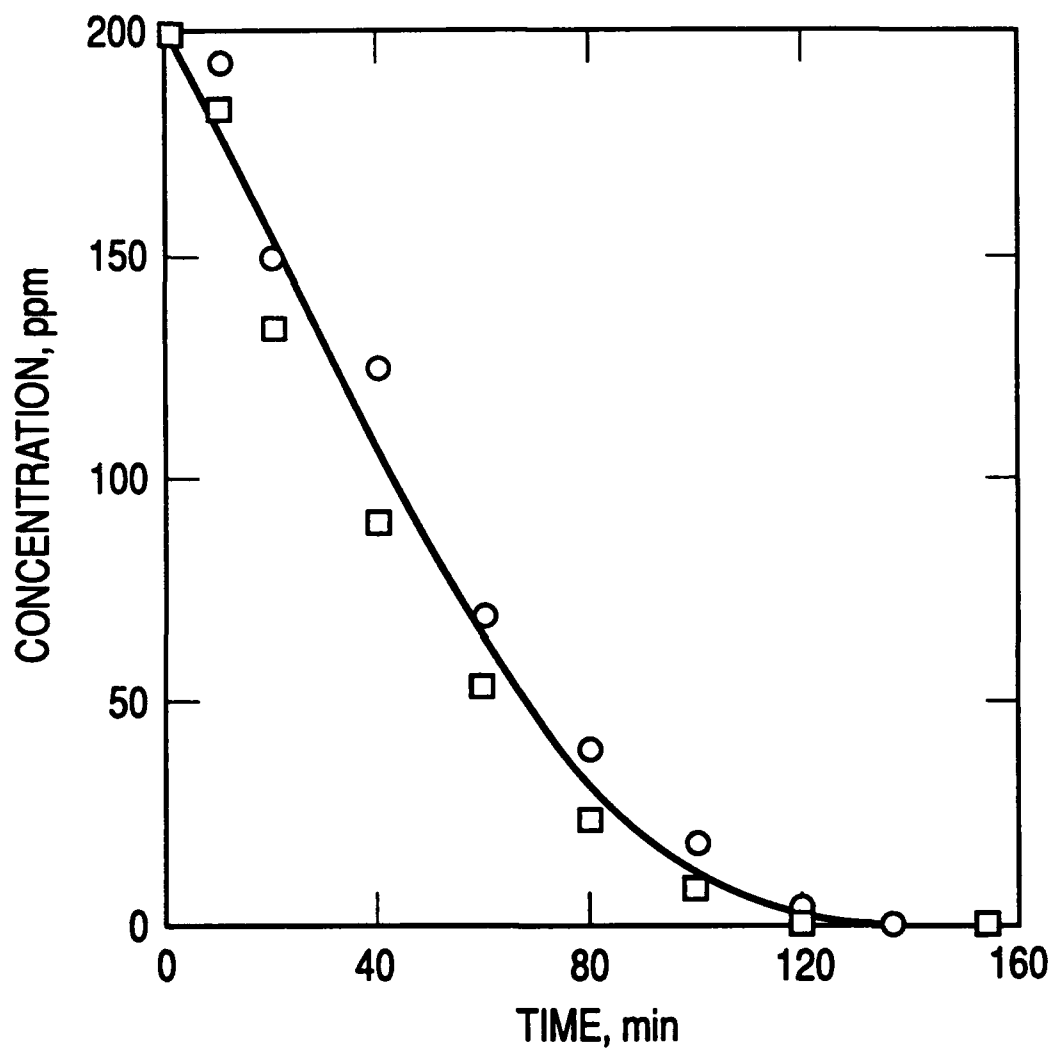
Figure 9. Ozone/uv treatment of toluene. Open circles and squares are data from two separate experiments.

III. Discussion

A. Literature Results

Previous literature results indicate that all of the hazardous wastes of interest, methyl and isopropyl alcohols, trichloroethylene and 1,1,1-trichloroethane (and chlorinated hydrocarbons in general), and benzene and substituted benzenes, should all be treatable in the HWWTS. In general, innocuous final products should result in all cases, provided the treatment is of sufficient duration. In the case of chlorinated hydrocarbons, small quantities of hydrochloric acid should result. This should not present any health or corrosion problems, provided the concentrations of waste to be treated do not exceed a few hundred ppm.

In most cases, the rate constants for direct ozone attack on the hazardous waste of interest (as well as on intermediate products formed by that ozone attack) are sufficiently low that ozone treatment alone could be prohibitively time consuming. For this reason, it is necessary to generate hydroxyl radicals from the ozone, which attack the materials of interest considerably more rapidly. In the HWWTS, this is done by circulating the hazardous waste water through a chamber containing uv lights, where the ozone is photolytically decomposed to form molecular oxygen and oxygen singlet D atoms. The oxygen singlet D atoms react with water to form hydroxyl radicals.

Hydroxyl radicals can also be formed by carrying out the waste treatment with alkaline solutions instead of uv light. In alkaline solutions, hydroxyl ions catalyze the formation of hydroxyl radicals from ozone. While this is feasible in principle, we have not carried out a critical evaluation of data from the literature to determine if it is practical. Without any acid or base treatment of solutions, the pHs will normally drift to the acidic side because of acidic reaction products that are formed during ozonolysis. Alkaline treatment to maintain generation of hydroxyl radicals from ozone, in place of uv light, would necessarily alter this drift to lower pH. This alteration, in turn, could alter reaction rates and even reaction mechanisms. What bearing this alteration would have on the conclusions discussed above regarding treatments of the various hazardous wastes is not known. Lacking this knowledge (indeed, the requisite information may not be available in the literature), the safest path may well be to treat the hazardous wastes

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discussed here by operating the HWWTS in the usual configuration, i.e., with uv lights and allowing the pH to drift.

B. Experimental Results

The experimental results for the methyl and isopropyl alcohols indicate that 100 ppm solutions of these materials should be readily treatable in the HWWTS with treatment times of 7 to 13 and 4 to 9 hr, respectively. Concentrations of a few hundred ppm, or treatment to levels much lower than 1 ppm, should not require excessively longer treatment times, due to the aggressive attack by hydroxyl radicals. In the field, it is likely that these alcohols would be present in dilute solutions of hydrazine propellant wastes, which would typically be treated for periods of 16 to 24 hrs (ref. 40). This extended treatment time should ensure destruction of the parent alcohols, and intermediate products formed from them, to levels well below 1 ppm. In addition, direct reactions of ozone with the hydrazines can lead to the production of free radicals that could further facilitate the destruction of the alcohols. Due to the high water solubilities of the alcohols and the low Henry's law constants, evaporative losses should be minimal. Extrapolation of our laboratory data indicates that evaporative losses of the alcohols in the HWWTS, averaged over the 16-24 hr treatment times, should not exceed 0.001 lb/hr. Indeed, even this is a worst case estimate, since it does not include attack on the alcohols by radicals produced from the decomposition of the hydrazine propellants. It also does not include potential and likely further decomposition that can occur in the ozone destruct unit on the vent stack of the HWWTS. This unit contains mixed catalytic metal oxides and is operated at temperatures of 140 to 150°F. Although the unit is designed to destroy ozone as gases are vented to the atmosphere, this destruction, and the elevated temperature, are likely to create a reactive environment that will also destroy other gases that are venting from the HWWTS. At this point, there are no data available to determine the potential magnitude of destruction of vent gases other than ozone.

It is likely that other water soluble gases or liquids with low Henry's law constants would behave similarly to the predictions for the methyl and isopropyl alcohols. Thus it is anticipated that a wide variety of such species can be readily treated in the HWWTS. Species

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that are less water soluble, having high Henry's law constants, should also be treatable, as indicated by the results obtained here for trichloroethylene, 1,1,1-trichloroethane, benzene, and toluene. For materials with limited water solubility, however, evaporative losses may compete with reaction losses for removal of the parent compounds from the HWWTS. (This is probably less likely with oxygenated intermediates formed from these parent compounds, since the intermediates are likely to be aldehydes, ketones, acids, etc., which probably have higher water solubilities than the parent compounds.)

Treatment of trichloroethylene, 1,1,1-trichloroethane, benzene, and toluene should require about 2-5 hr in the HWWTS, depending upon the compound. About half of the loss will be due to evaporation. If, as anticipated, these materials are mixed with hydrazine fuel wastes, average emissions over a 16-24 hr treatment time will be 0.05-0.08 lb/hr, for a worst case assumption (Henry's law constant of 200 atm/mole fraction). Additional factors that are likely to reduce these emissions are similar to those discussed above, namely, cross reactions involving radicals generated from ozone attack on the hydrazines and potential decomposition in the ozone destruct unit. These same factors probably also apply to other materials with limited water solubilities and high Henry's law constants.

If solutions of trichloroethylene, 1,1,1-trichloroethane, benzene, and/or toluene (or other organics with limited water solubility and high Henry's law constants) are to be treated individually (not mixed with hydrazine propellant wastes), some modified treatment procedures may be considered. In such cases, especially since ozone consumption appears to be small for these species, lowering the ozone/oxygen flow rate (or injecting ozone intermittently) may be beneficial in increasing the chemical destruction losses and lowering the evaporative losses. Another alternative might be to use hydrogen peroxide and uv instead of ozone/uv and run with water recirculation only and no gas injection. (However, the vent to the atmosphere should remain open to alleviate any pressure buildup due to the production of carbon dioxide or any other volatile gases.) Although this procedure may be less desirable from the standpoint of needing to store concentrated solutions of hydrogen peroxide, it might be acceptable if a specific waste is known to be

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generated on some future date and a limited, small quantity of hydrogen peroxide can be obtained on short order from a vendor.

In conclusion, it appears that water soluble organic wastes can readily be treated in the HWWTS with ozone/uv. With organic contaminants possessing limited water solubility and high Henry's law constants, some evaporative losses can occur. In a worst case, these losses, for initial concentrations of 100 ppm, will be of the order of 0.05 to 0.08 lb/hr, averaged over the 16-24 hr treatment time. Additional potential reaction paths and/or modification of operating procedures could substantially reduce the evaporative losses.

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90-3525-HHT-21
5 April 1990

Subject: Ozone UV Destruction of Organic Contaminants

To: HQ Space Systems Division (Capt. K. Held SSD/CLR)
           Los Angeles Air Force Base
           Los Angeles, CA 90009

1. Attached is a laboratory study test plan for the ozone UV detoxification of organic contaminants, found in launch deluge waste waters. This study, to be conducted by H. Judeikis of the Aerospace Laboratory, should provide data that will be useful for processing organic contaminants with the VAFB Prototype Hydrazine Waste Water Treatment System. The selection of contaminants and concentrations to be tested was made together with VAFB personnel.

H. H. Takimoto
Chemical Systems Directorate
Western Test Range
Space Launch Operations

Atch

cc: W. Freed
    H. Judeikis
    S. Lewis
    D. Nichols
    F. Sobottka

A-1

TEST PLAN

Ozone UV Destruction of Organic Contaminants

1.0 Objective

The objective of this Aerospace Laboratory bench scale study is to determine
the effectiveness of the ozone UV treatment process for the conversion of
organic contaminants, present in space launch generated waste waters, into
innocuous materials. Small quantities of these contaminants are found in the
waste water together with hydrazines and a treatment method for their safe
disposal capable of satisfying regulatory requirements is needed. The
specific objective of this study is to establish test parameters for the ozone
UV detoxification process that will be useful for processing organic
contaminated water with the VAFB Prototype Hydrazine Waste Water Treatment
System.

2.0 Scope

This study will investigate the ozone UV treatment of aqueous solutions of
compounds such as the following but not to the exclusion of others:

Methyl alcohol   Isopropyl alcohol
1,1,2-Trichloroethylene   1,1,1-Trichloroethane
Xylenes

If the greenish-black contaminant, observed in the WSTF performance test is
available, it also will be included in the test series.

Before initiation of the laboratory tests, a literature survey of previous
studies conducted on the ozone UV detoxification of organic materials in
aqueous solution will be conducted. Since this treatment method has been used
for water purification, it is anticipated that data pertinent to the present
study should be available. The literature information should serve as a
guideline for specific test conditions to be investigated. The tests will
determine parameters such as the following:

A   The effect of UV on the rate of decomposition and quality of the
      treated water.

B.   The process time required to produce environmentally acceptable
      treated water.

C.   Analysis techniques to verify complete destruction of the
      organic compounds and reduction of the intermediate oxidized
      product concentration down to environmentally acceptable levels.

D.   Determination of the volatiles released during the treatment
      process.

3.0 Experimentations

Synthetic test solutions containing appropriate concentrations of organic contaminants will be prepared. A laboratory system will be designed to model the process section of the VAFB Prototype Hydrazine Waste Water Treatment System. The oxidative degradation of the contaminants may initially be investigated individually to determine their rates of disappearance as well as to identify the products that are generated. However, later runs will utilize a mixture of selected contaminants to see whether the presence of several components will alter the course of the reaction, thereby affecting the decomposition rates and/or the products that are formed. The concentrations of the contaminants in the simulated waste waters to be tested will be in the 25 to 100 mg/liter range.

If the dark greenish black contaminant found in the VAFB launch water transported to WSTF for the performance tests of the Prototype Hydrazine Waste Water Treatment System could be obtained, it will also be included in this laboratory test series.

4.0 Chemical Analysis

The treated water will be analyzed to insure that the contaminants have been completely destroyed and that no hazardous intermediate products are remaining in the test solution. The effluent gas stream shall be analyzed for volatile constituents that might escape from the reaction mixture. If cold traps are to be used, their temperature should be carefully controlled to insure that only the volatiles from the reaction mixture are accumulated without trapping the explosive ozone.

5.0 Report

A report on the test results will be prepared. This document will provide a detailed description of the tests, a discussion of the results and an evaluation regarding the applicability as well as the limitations of the VAFB Prototype Hydrazine Waste Water Treatment System in processing organic contaminants commonly found in space launch generated waters.

DEPARTMENT OF THE AIR FORCE
HEADQUARTERS 1ST STRATEGIC AEROSPACE DIVISION (SAC)
VANDENBERG AIR FORCE BASE, CALIFORNIA 93437-5000

REPLY TO ATTN OF ET

13 JUN 1990

SUBJECT Ozone/Ultraviolet Light Oxidation Wastewater Treatment System at Space Launch Complex 6 (SLC-6)

TO WSMC/SUO

1. The ozone/ultraviolet light oxidation system is designed to treat only nonhazardous wastewaters containing hydrazine. In looking ahead, this system could be useful in the treatment of wastewaters containing certain organic constituents (1,1,1 trichloroethane, trichloroethylene, methylene chloride, methyl ketone, toluene, benzene) which are sometimes generated by our contractors. We request that the above listed chemicals be reviewed and tested to determine if they could be effectively treated by the system.

2. We would appreciate three copies of the design specifications, the data from the White Sands test trials, laboratory analyses (including EPA test methods used), and the standard operating procedures for the system.

3. During our upcoming meeting with the Environmental Protection Agency and California Department of Health Services, we will be preparing questions concerning land disposal restrictions, permit requirements, and treatment standard requiring regulatory interpretation. We welcome your input. Our POC is Roberta Tassey or Lt Col John Sipos, 6-5724.

ORVILLE G. ROBERTSON, Colonel, USAF
Director, Environmental Management

TECHNOLOGY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security programs, specializing in advanced military space systems. The Corporation's Technology Operations supports the effective and timely development and operation of national security systems through scientific research and the application of advanced technology. Vital to the success of the Corporation is the technical staff's wide-ranging expertise and its ability to stay abreast of new technological developments and program support issues associated with rapidly evolving space systems. Contributing capabilities are provided by these individual Technology Centers:

Electronics Technology Center: Microelectronics, solid-state device physics, VLSI reliability, compound semiconductors, radiation hardening, data storage technologies, infrared detector devices and testing; electro-optics, quantum electronics, solid-state lasers, optical propagation and communications; cw and pulsed chemical laser development, optical resonators, beam control, atmospheric propagation, and laser effects and countermeasures; atomic frequency standards, applied laser spectroscopy, laser chemistry, laser optoelectronics, phase conjugation and coherent imaging, solar cell physics, battery electrochemistry, battery testing and evaluation.

Mechanics and Materials Technology Center: Evaluation and characterization of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; development and analysis of thin films and deposition techniques; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; development and evaluation of hardened components; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion; spacecraft structural mechanics, spacecraft survivability and vulnerability assessment; contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; lubrication and surface phenomena.

Space and Environment Technology Center: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation; propellant chemistry, chemical dynamics, environmental chemistry, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes, and sensor out-of-field-of-view rejection.